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The Effect of 3-aminopropyltrimethoxysilane (AMEO) as a Coupling Agent on Curing and Mechanical Properties of Natural Rubber/Palm Kernel Shell Powder Composites

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Abstract

This research is conducted using palm kernel shell powder (PKS) as filler in natural rubber. The effect of 3-aminopropyltrimethoxysilane as coupling agent on composites were studied at different palm kernel shell loading i.e, 0, 5, 10, 15 and 20 phr. The palm kernel shell was crushed and sieved to an average particle size of 5.53 μm . The palm kernel shell filled natural rubber composites were prepared using laboratory size two roll mill. The curing characteristics such as scorch time, cure time and maximum torque were obtained from rheometer. The palm kernel shell powder filled natural rubber composites were cured at 150°C using hot press according to their cure time. Curing characteristics, tensile properties, rubber-filler interaction and morphological properties of palm kernel shell powder filled natural rubber were studied. Scorch time and cure time show reduction but tensile strength, elongation at break, modulus at 100% (M100) and modulus at 300% (M300) increased with the presence of 3-aminopropyltrimethoxysilane. Rubber-filler interaction studies showed that rubber filler interaction in natural rubber filled with palm kernel shell powder improved with incorporation of 3-aminopropyltrimethoxysilane.

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Keywords: Palm kernel shell; 3-aminopropyltrimethoxysilane; Tensile strength; Morphology

1. Introduction

Natural rubber with chemical name 1,4 cis-isoprene can crystallize on stretching or cooling due to its microstructure consisting entirely of cis form of isoprene. The higher degree of crystallinity of rubber, the higher is the gum strength. The ability of natural rubber to strain crystallized affect the magnitude of gum strength for example good tensile strength and tear strength. The intrinsic high gum strength can be utilized to its advantage by incorporating large quantity of cheap fillers to reduce compounding cost ¹. Moreover, fillers also added to modify and improve specific properties desired ². Nowadays, natural fillers have become widely known among rubber technologists because of their advantages. Due to global demand for environmental friendly products, immense research works have been carried out to investigate the use of natural fillers in rubber composites and their potential to be marketed. Natural fillers are environmentally friendly, fully degradable, readily, abundantly available, cheap and have low density ³. However, the disadvantages of natural fillers are their polarity. Hydrophilic nature of natural fillers results in incompatibility with natural rubber which is hydrophobic ⁴. Other problems with natural fillers are their tendency to form agglomerates during processing and also poor resistance to moisture. This problem retards the potential of natural fillers to be used as reinforcing filler in composites ⁵.

The incorporation of cellulosic fillers into polymers will result in poor dispersion due to strong hydrogen bonding that hold the fiber or filler together ⁴. The solutions to this drawback are by incorporating silane coupling agents or by using surface treatment methods to improve the degree of wetting of natural filler by polymer and promotes interfacial adhesion ⁶. Coupling agent has bi- functional groups that form linkages between natural filler and polymer matrix that resulted in better interfacial adhesion between them ⁷. There are abundance of natural fiber and filler resources such as rattan, wood flour, betel, pineapple leaves, kenaf, bamboo, etc in Malaysia. Palm oil was one of them. Palm oil was harvested from palm oil tree and after that the palm trees are burnt off, disposed or turned into biomass fuel ⁸. This action can lead to serious environmental and health problems such as haze, water pollution and respiratory diseases. There are a few research has been done to study the possible application from waste of palm oil ⁹⁻¹². The aim of this research is to use palm kernel shell as potential filler in rubber and polymer industry. The objective of this work is to study the curing and mechanical properties of palm kernel shell filled natural rubber composites as function of filler loading and silane (3-aminopropyltrimethoxysilane) as coupling agent.

2. Experimental

2.1 Materials and chemicals

Table 1 shows the materials, their suppliers and amount used in this study. The palm kernel shell (PKS) used in this work belongs to the species of *Elais Guineensis*. The palm kernel shell were collected, grounded and sieved into average particle size of 5.53 µm. Table 2 shows the elemental composition of PKS in this study.

Nomenclature

CBS	n-cyclohexyl-2-benzothiazolsulfenamide
TMTD	tetra-methyl-thiuramdisulphide
BKF	2,2- methylene-bis-(4-methyl-6-tert-butylphenol)
AMEO	3-aminopropyltrimethoxysilane
RRIM	Research Institute of Malaysia Rubber

Table 1. Formulation of PKS-filled natural rubber composites.

Ingredients	Formulation (phr)		Suppliers
	Series 1	Series 2	
SMR L	100	100	RRIM ^e
Palm kernel shell	0, 5,10,15,20	5, 10,15,20	United Oil Palm Industries Ltd
Zinc Oxide	5	5	Bayer (M) Ltd
Stearic Acid	3	3	Bayer (M) Ltd
CBS	0.5	0.5	Bayer (M) Ltd
TMTD	0.1	0.1	Bayer (M) Ltd
BKF	1	1	Bayer (M) Ltd
Sulphur	2.5	2.5	Bayer (M) Ltd
Silane coupling agent (AMEO)	-	1.0	Bayer (M) Ltd

Table 2. Chemical and elemental composition of PKS.

	Properties	Approximate value (%)
Chemical composition	Moisture content (wt)	6.2
	Ash content	8.7
	porosity	27
	Hemi cellulose	26.2
	Cellulose	7.2
	Lignin	54.2
Elements	C	86.63
	Fe ₂	3.7
	CaO	3.5
	SiO	3.5
	Al ₂ O ₃	0.9
	Cl	0.5
	CrO ₄	0.3
	P ₂ O ₅	0.2
	SO ₃	0.2
	Mg	0.2
	ZnO	0.1
	Trace elements	3.7

2.2 Sample Preparation

Sieved palm kernel shell powder was dried in an oven at 100°C for 1 hour to expel moisture. Mixing was carried out using laboratory two roll mill size (160 × 320 mm²) according to ASTM designation D3184-80. The first series was without silane coupling agent and the second series was with silane coupling agent. Nip gap, mill roll speed ratio, time of mixing and the sequences of addition of the ingredients was kept constant for all composites. Stearic acid, zinc oxide, accelerators, followed by filler, antioxidant and finally sulphur were added orderly. The sheeted rubber compounds were cut and cure assessment was carried out using Monsanto moving die rheometer (model MDR 2000) at 150°C. Cure time (t_{90}), maximum torque (M_H), scorch time (ts_2) were obtained from the torque versus time rheographs. The rubber compounds were molded into sheets with respective cure time (t_{90}) at 150°C using hot press machine.

2.3 Measurement of Tensile Properties

The stress-strain properties of PKS filled natural rubber composites such as tensile strength, elongation at break, modulus at 100% and 300% elongation were measured using Instron Universal Testing machine (model 3366) at test temperature of 23°C according to ASTM D412 at 500 mm/min crosshead speed.

2.4 Swelling Test

Swelling test was performed to determine rubber-filler interaction (Q_f/Q_g) according to Lorenz Park equation and cross link density according to Flory-Rehner equation. The vulcanized sample (30mm × 5mm × 2mm) was weighed and allowed to swell in solvent (toluene) for 72 hours at room temperature (25°C). After 72 hours, the samples were removed, wiped and weighed. The samples were then dried in an oven at 70°C until constant weight was obtained. As for crosslink density, the sample was weighed and allowed to swell in toluene until equilibrium swelling is obtained. On the attainment of equilibrium, the samples removed and quickly wiped and weighed. The sample dried in an oven at 70°C until constant weight was obtained.

2.5 Scanning electron microscopy (SEM)

Examination of the tensile fracture surface was carried out using a scanning electron microscope, model Zeiss Supra 35vp. The fracture part of tensile specimens were used. The fracture surfaces were sputter coated with gold to avoid electrostatic charging and poor image resolution. The images of rubber and filler dispersion were evaluated from the micrographs.

3. Results and discussion

3.1 The effect of silane coupling agent, AMEO on curing characteristics

Table 3 shows the effect of PKS loading and silane coupling agent, AMEO on scorch time (ts_2), cure time (t_{90}) and maximum torque. The scorch time and cure time results in Table 3 show a decreasing value as increase in filler loading. Shorter ts_2 and t_{90} are caused by premature curing due to shearing force generated during compounding process. As the filler loading increases, the time of incorporation of additives and filler also increased. Excessive heat accumulated from longer compounding time. The significant decrease also can be seen in ts_2 and t_{90} of composites with silane coupling agent. The decrease in ts_2 and t_{90} are affected by the increasing amount of sulphur content in the composites by addition of silane coupling agent. The presence of extra sulphur will accelerate the curing rate of the rubber composites¹³. Maximum torque (M_H) determine the stiffness or shear modulus of rubber composite at its vulcanization temperature¹⁴. As shown in Table 3 M_H increased with increasing of PKS loading. This is due to addition of hard and rigid PKS particles into soft and rubbery matrix. This limited the movement of macromolecular rubber chains. The more inclusion of filler, the more restriction undergo by rubber chains. This resulted rubber composites became harder and stiffer¹⁵. This phenomenon also cause weariness during mixing process^{7,16}. At similar PKS loading, M_H of NR composites with silane coupling agent are higher compared to PKS filled NR composites without silane coupling agent. Sulphur atoms in silane coupling agent assist in increasing elemental sulphur contents in rubber composites which increase crosslink density¹⁷. As values of M_H increases, the crosslink density is also expected to increase¹⁸.

Table 3. Variation of scorch time (t_{s2}), cure time (t_{90}), and maximum torque (M_H) of PKS filled natural rubber composites with and without silane coupling agent.

Sample code	Scorch time (min)	Cure time (min)	Maximum torque (dNm)
Gum NR	2.6	4.91	7
NR/PKS 5	2.66	4.88	7.15
NR/PKS 10	2.67	4.86	7.57
NR/PKS 15	2.65	4.82	7.98
NR/PKS 20	2.62	4.80	8.31
NR/SPKS 5 *	1.74	4.75	7.4
NR/ SPKS 10	1.46	3.5	7.87
NR/SPKS 15	1.40	3.4	8.4
NR/SPKS 20	1.28	2.99	8.89

NR/SPKS: composite with silane coupling agent

3.2 The effect of silane coupling agent, AMEO on mechanical properties

Table 4 shows the effect of silane coupling agent on tensile properties of PKS filled NR composites. According to Table 4, the tensile strength of PKS filled NR composites decrease with increasing filler loading. As filler loading increases, the filler cannot longer be wetted by matrix. The filler form agglomerates that lead to poor physical contact with neighboring aggregates. The reduction of tensile strength is also due to the inferior adhesion and incompatibility between PKS and rubbery matrix. Poor adhesion of the filler and rubber matrix is caused by different polarity. The hydrophilic nature of filler tend to distribute unequally and form agglomerates on non polar polymer matrix⁴. However, there is an increase in tensile strength of PKS filled NR composites with silane coupling agent compare to PKS filled NR composites without silane coupling agent. Other researchers also reported similar result in their studies^{7,13,19,20}. The hydrophilic nature of filler surface can be modified into hydrophobic by using silane coupling agent²¹. Silane coupling agent capable of binding active chemical group of the polymer by forming chemical bond between filler and matrix. This makes silane coupling agent an efficient medium to improve interfacial adhesion and compatibility between filler and rubber matrix. The incorporation of silane coupling agent can improves mechanical properties of natural rubber composites filled with natural fillers. It can improves interfacial adhesion and stress distribution between filler and rubber matrix. The theory and mechanism of reinforcement explains more about load sharing effect imparted by filler that lead to high tensile strength. Fillers are connected to the molecular network chains of the matrix by attachment of a few adjacent molecules to one filler particle. When highly stressed, molecular chain break and the tension is transferred to adjacent number of other chains via filler particles. As a result, the composites resist detachment during tensile test as the filler attached strongly to rubber matrix with the assistance of silane coupling agent²².

Elongation at break (E_b) reduces as increasing in filler loading. Increase in filler loading stiffens and hardens the compounds and cause reduction in its flexibility. Moreover, natural fillers are non-deformable. As further increase in filler loading reduces the deformable rubber part in the composites. However, E_b for the composites with silane coupling agent are higher as compared to E_b composites without silane coupling agent. The presence of silane coupling agent promotes better dispersion of the filler and adhesion between filler and rubber matrix. Silane coupling agent reduces E_b of the composites as it result in more rigid composites. The opposite trend was observed for tensile moduli of PKS/NR composites with and without addition of silane coupling agent. Tensile modulus at 100% (M100) and 300% (M300) increased with increasing filler loading. Moreover, M100 and M300 also improved for composites with silane coupling agent as shown in Table 4. The presence of silane coupling agent also reduces the chain mobility and increase rigidity of the composites. Thus, exhibit high tensile modulus of the composites²³.

Table 4. Tensile Properties of NR/PKS filled composites with and without silane coupling agent.

Sample code	Tensile strength (MPa)	Elongation at break (%)	M100 (MPa)	M300 (MPa)
Gum NR	20.43	863.9	0.8209	2.1797
NR/PKS 5	19.753	846.667	0.937	2.206
NR/PKS 10	16.627	799.433	1.0755	2.512
NR/PKS 15	14.640	781.133	1.1357	2.714
NR/PKS 20	11.740	747.2	1.09	2.715
NR/SPKS 5	20.820	913.333	0.786	2.433
NR/SPKS 10	19.487	859.433	0.993	2.621
NR/SPKS 15	18.853	877.233	0.994	2.804
NR/SPKS 20	18.703	847.767	1.173	3.091

3.3 Swelling properties

The cross link density of PKS filled NR composites with and without silane coupling agent can be observed in Table 5. The degree of adhesion between filler and rubber matrix can be obtained from swelling of samples in a solvent ²⁴. The addition of silane coupling agent distinctly improves the extent of adherence between filler and rubber matrix as silane coupling agent able to weaken filler-filler bond and strengthen filler-rubber interaction in the composites. The rubber-filler interaction (Q_f/Q_g) values for composites with silane coupling agent increased as increase in filler loading. It is known that higher Q_f/Q_g values indicate lower interaction between rubber matrix and filler used and vice versa. The increase in toluene uptake show that low rubber-filler interaction as results of few cross links formed per rubber chain. . It also caused by polarity of ligno cellulosic nature of filler which tend to absorb solvents on its surface ⁷. This is due to the fact that cellulose content in natural filler has hydroxyl group on its surface, which produces strong hydrogen bonding. However, rubber- filler interaction has improved with incorporation of silane. This is due to fact that silane coupling agent improves interaction between filler and rubber matrix.

Table 5. Swelling percentage, rubber-filler interaction (Q_f/Q_g) and cross link density of NR/PKS composites.

Sample code	Swelling percentage (%)	Q_f/Q_g	Cross link density ($\times 10^{-5}$ g/cm ³)
Gum NR	348.255	1.0000	7.4290
NR/PKS 5	334.646	1.0187	7.7500
NR/PKS 10	334.147	1.0543	7.7120
NR/PKS 15	325.982	1.1706	7.7800
NR/PKS 20	289.144	1.1823	9.3580
NR/SPKS 5	345.827	0.9081	7.5870
NR/SPKS 10	286.409	0.9117	7.9970
NR/SPKS 15	275.863	0.9785	10.3600
NR/SPKS 20	256.829	0.9980	11.8860

3.4 Surface Morphology Study

SEM micrographs of PKS filled NR composites with and without silane coupling agent are shown in Fig.1 and 2. It can be observed that the surface fracture of PKS filled NR composites with silane coupling agent have less detachment due to strong interfacial adhesion between filler and rubber matrix (Fig 1(a) and (b)). The fracture surfaces show rough zones and deeper tearing lines indicate high stress rupture. The incorporation of silane coupling agent improves the adhesion between filler and rubber matrix. However, poor adhesion is reflected in PKS filled NR

composites as the fractured surface of the samples show more detachment of filler without addition of silane coupling agent (Fig 2(a) and (b)). At higher filler loading (20 phr), the filler tend to agglomerate and this cause major failure in mechanical properties of the composites.

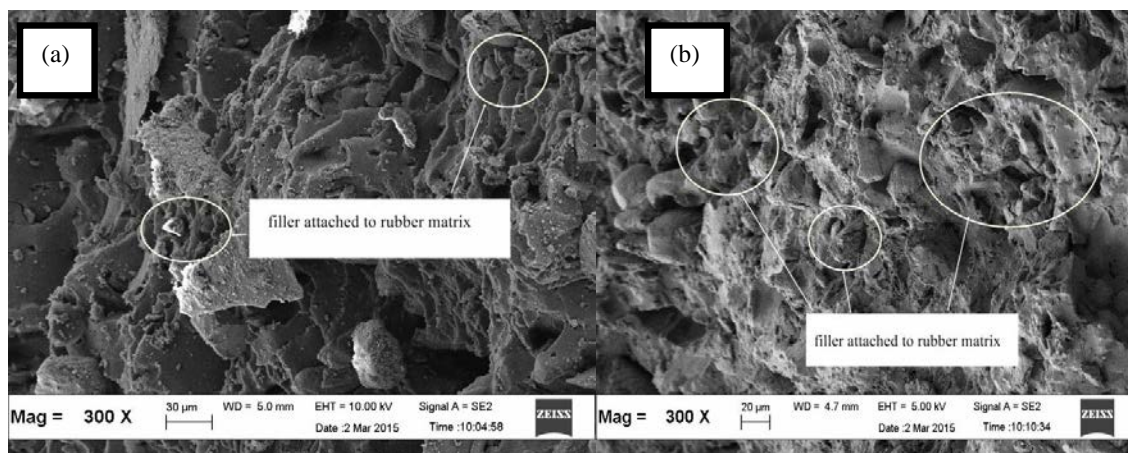


Fig 1. Micrographs of PKS filled NR composites with silane coupling agent (a) 10 phr ;(b) 20 phr PKS loading.

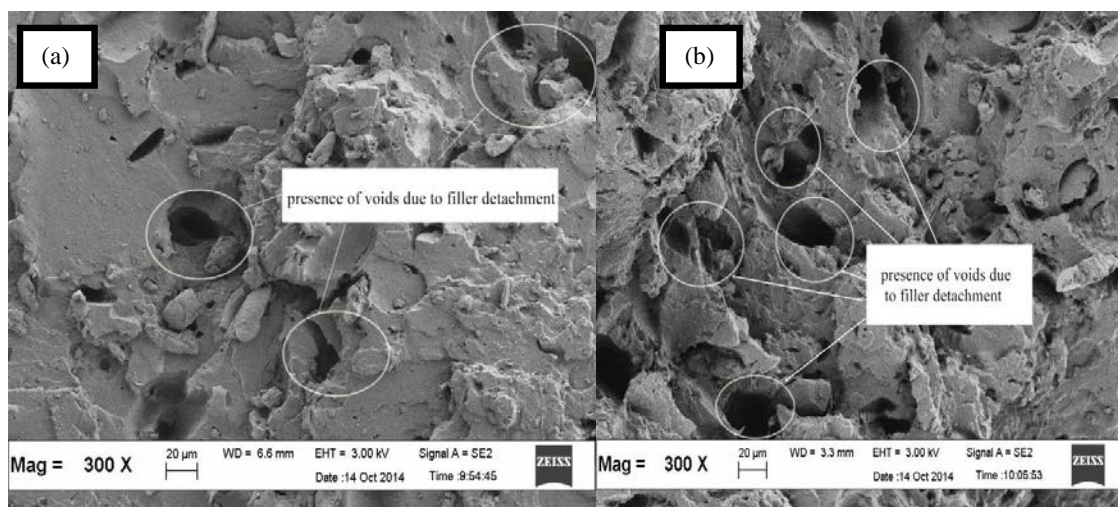


Fig. 2. Micrograph of PKS filled NR composites without silane coupling agent (a) 10 phr ;(b) 20 phr PKS loading.

4. Conclusion

The curing characteristics of PKS filled NR composites showed that the scorch time (t_{s2}) and cure time (t_{90}) decreased but maximum torque (M_H) increased with the presence of silane coupling agent in the composites. The tensile strength, elongation at break and tensile modulus increased with addition of silane coupling agent, AMEO. The cross link density and rubber-filler interaction were also improved. It can be concluded that silane coupling agent overall enhance the mechanical properties of NR/PKS composites.

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6. References

1. Joshi SV., Drzal LT, Mohanty AK, Arora S. Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Compos Part A Appl Sci Manuf* 2004;**35**(3):371-376.
2. Ku H, Wang H, Pattarachaiyakoo N, Trada M. A review on the tensile properties of natural fiber reinforced polymer composites. *Compos Part B Eng* 2011;**42**(4):856-873.
3. Komethi Muniandy, Hanafi Ismail NO. Studies on natural weathering of rattan powder- filled natural rubber composites. *Compos* 2012;**7**:3999-4011.
4. Xie Y, Hill CS, Xiao Z, Militz H, Mai C. Silane coupling agents used for natural fiber/polymer composites: A review. *Compos Part A Appl Sci Manuf* 2010;**41**(7):806-819.
5. Saheb DN, Jog JP. Natural Fiber Polymer Composites : A Review. 1999;**18**(4):351-363.
6. Muniandy K, Ismail H, Othman N. Biodegradation, morphological, and fir study of rattan powder-filled natural rubber composites as a function of filler loading and a silane coupling agent. *BioResources* 2012;**7**(1):957-971.
7. Ismail H, Santiagoo RKH. Mechanical properties, water absorption, and swelling behaviour of rice husk powder filler polypropylene/ recycled acrylonitrile butadiene rubber biocomposites using silane as a coupling agent. *bioresources.com* 2011;**6**:3714-3726.
8. Abdul Khalil, Poh BT, Issam A.M, Jawaid M, Ridzuan R. Recycled Polypropylene-Oil Palm Biomass: The Effect on Mechanical and Physical Properties. *J Reinf Plast Compos* 2010;**29**(8):1117-1130.
9. Egwaikhide PA, Akporhonor EE, Okiemen FE. An Investigation on the Potential of Palm Kernal Husk as Fillers in Rubber Reinforcement. 2007;**2**(1):28-32.
10. Shaari Ismail HSM. the effect of Chitosan on the curing chracteristics, Mechanical and morphological properties of chitosan-filled NR, ENR, and SBR compounds. *Elsevier*.
11. Jacob M, Thomas S, Varughese KT. Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites. *Compos Sci Technol* 2004;**64**(7-8):955-965.
12. Ratim S, Ahmad S, Rasid R. [AMN08] Effect of the silane coupling agent on the hybrid thermoplastic natural rubber composites filled rice husk and oil palm empty fruit bunch Blends of TPNR matrix were first prepared with composition ratio of NR : LNR : HDPE are 20 : 10 : 70 vol . *Semin Natl Sci Fellowsh* 2004:334-339.
13. Ismail H, Mahir NA, Ahmad Z. The Effect of Bis-(3-triethoxysilylpropyl) Tetrasulphide (Si-69) as a Coupling Agent on Properties of Natural Rubber/Kenaf Fibre Composites. *Polym Plast Technol Eng* 2011;**50**(9):893-897.
14. Nabil H, Ismail H, Azura a. R. Comparison of thermo-oxidative ageing and thermal analysis of carbon black-filled NR/Virgin EPDM and NR/Recycled EPDM blends. *Polym Test* 2013;**32**(4):631-639.
15. Ismail H, Edyham MR, Wirjosentono B. Bamboo fibre filled natural rubber composites: The effects of filler loading and bonding agent. *Polym Test* 2002;**21**(2):139-144.
16. Ismail H, Nasaruddin MN, Rozman HD. The effect of multifunctional additive in white rice husk ash ® lled natural rubber compounds. 1999;**35**:1429-1437.
17. Choi SS. Influence of rubber composition on change of crosslink density of rubber vulcanizates with EV cure system by thermal aging. *J Appl Polym Sci* 2000;**75**(11):1378-1384.
18. Hayeemasae N, Ismail H, Azura AR. Blending of Natural Rubber/Recycled Ethylene-Propylene-Diene Monomer: Cure Behavior and Mechanical Properties. *Polym Plast Technol Eng* 2013;**52**(October 2014):501-509.
19. Ismail H, Mega L, Abdul Khalil HPS. Effect of a silane coupling agent on the properties of white rice husk ash-polypropylene/natural rubber composites. *Polym Int*. 2001;**50**(5):606-611.
20. Ismail H, Shaari SM. Curing characteristics, tensile properties and morphology of palm ash/halloysite nanotubes/ethylene-propylene-diene monomer (EPDM) hybrid composites. *Polym Test*. 2010;**29**(7):872-878.
21. Marciniac B, Krysztafkiewicz A, Domka L. Wettability of silane films on silica fillers. *Colloid Polym Sci* 1983;**261**(4):306-311.
22. Samsuri A. Theory of Mechanism of Reinforcement. In: *Natural Rubber Materials* 2004:79.
23. Ismail H, Jaffe RM. Curing Characteristics and Mechanical Properties of Oil Palm Wood Flour Reinforced Epoxidized Natural Rubber Composites. *Int J Polym Mater* 1997;**36**(3-4):241-254.
24. Rice AFA, Costa HM, Nunes RCR, Visconte LLY. Physical Properties and Swelling of Natural Rubber Compounds Containing Rice Husk Ash. *Raw Mater Appl*. 2001; (5):242-249.